Structural and optical properties of $Nd_xGd_{1-x}Cr_3(BO_3)_4$ solid solutions

E.A. Dobretsova[1,2,*], K.N. Boldyrev[1], E.Yu. Borovikova[3], and V.A. Chernyshev[4]

[1]Institute of Spectroscopy RAS, 108480 Troitsk, Moscow, Russia
[2]P.N. Lebedev Physical Institute RAS, 119991 Moscow, Russia
[3]M.V. Lomonosov Moscow State University, 119991 Moscow, Russia
[4]Ural Federal University, 620002 Ekaterinburg, Russia

Abstract. The spectroscopic investigation of the solid solutions $GdCr_3(BO_3)_4$ (sp.gr. *R*32) – $NdCr_3(BO_3)_4$ (sp.gr. *C*2/*c*) is presented. The single crystals $Nd_xGd_{1-x}Cr_3(BO_3)_4$, $0 \le x \le 1$ with the step of 0.1, were grown by a flux method. Crystal structures were identified by terahertz and optical spectroscopy methods. *Ab initio* calculations in the frame of density functional theory allowed us to separate modes belonging to the *R*32 and *C*2/*c* phases and to estimate the ratio of these phases in $Nd_xGd_{1-x}Cr_3(BO_3)_4$ crystals. Content of the monoclinic phase (C2/c) increases with growth of the Nd concentration.

The borate family with a general formula $RM_3(BO_3)_4$ (*R* stands for Y or rare-earth (RE) elements, *M* = Al, Fe, Cr, Ga, Sc, Mn) has wide variety of physical properties depending on chemical composition and growth conditions. The borate crystals are well known as functional materials, and they are thermally and chemically stable. They are perspective for applications due to their optical, magnetic and magnetoelectric properties. Magnetic properties of RE borates with the magnetic ions Fe^{3+} and Cr^{3+} are of fundamental interest due to a coexistence and interaction of two magnetic subsystems (3*d* and 4*f* ions). Moreover, interaction in the iron (chromium) subsystem has quasi-one-dimensional character. Though there is a lot of research on the iron borates, the RE chromium borates are still understudied [1-3]. The analysis of thermal, magnetic, and optical properties of $NdCr_3(BO_3)_4$ has shown that the compound orders antiferromagnetically into an easy-plane magnetic structure at the temperature T_N=8 K [1]. The RE chromium borates have polytypic nature and, depending on growth conditions, crystallize in two modifications, namely, a non-centrosymmetric rhombohedral one with the space group *R*32 and a centrosymmetric monoclinic one with the space group *C*2/*c* [4, 5]. Coexistence of differently ordered fragments in a single crystal is a characteristic feature of these compounds.

In this paper, we show results of solid solutions $GdCr_3(BO_3)_4$ (sp.gr. *R*32) – $NdCr_3(BO_3)_4$ (sp.gr. *C*2/*c*) investigation by terahertz and optical spectroscopy methods. The purpose of our investigation was to trace the behaviour of the borate crystal structure at the substitution of Gd by Nd. On the ground of the results on the iron borates [6], we suppose

* Corresponding author: elena-dobrecova@yandex.ru

that the compound with maximum content of Nd and primary rhombohedral non-centrosymmetric crystal structure will demonstrate a maximum magnetoelectric response.

We have measured absorbance spectra of $Nd_xGd_{1-x}Cr_3(BO_3)_4$ borates in the range of the ${}^4I_{9/2} \rightarrow {}^4F_{3/2}$ electronic transition in the Nd^{3+} ion. For the samples with $x<0.6$, at temperature T=16 K> T_N, we observe two spectral lines (corresponding to the transitions from the ground Kramers doublet to the two CF levels of ${}^4F_{3/2}$). For $x>0.6$, the lowest-frequency spectral line splits into two components. Because the temperature of magnetic ordering of the chromium borates is lower than 16 K [1], this splitting is not related to a splitting of Kramers doublets in an internal magnetic field. Thus, in the case of Nd^{3+} ion concentration more than 60% in the solid solutions, the frequencies of this line for the rhombohedral and monoclinic phases are different. We can estimate a structural phases' ratio in the crystals. The more intensive line represents the monoclinic phase and the less intensive one – the rhombohedral phase.

The terahertz range of IR spectra displays vibrations of the RE ions. The main change when changing x is in intensity redistribution between bands with frequencies ~ 70 cm^{-1} and 77 cm^{-1} related to the monoclinic and rhombohedral phases, respectively. In the spectrum of $GdCr_3(BO_3)_4$, the band 77 cm^{-1} has a shoulder 70 cm^{-1} which is due to a small admixture of the monoclinic phase. Decomposition of the spectrum into two Gaussians shows that the intensity of the stronger band is above 80%. According to the *ab inito* calculations, the oscillator strength of the vibration in the monoclinic phase is 1.5 times larger than that of the rhombohedral one. Considering this, we estimate the rhombohedral phase content as about 85%. We observe a large content of the monoclinic phase (above 40% taking into account the oscillator strengths) already in the case of 20% Nd concentration in the crystals. If the Nd concentration is more than 70%, the low-frequency bands of the rhombohedral and the monoclinic phases coincide. For this reason, it is impossible to distinguish the structural phases in terahertz range for these compositions.

Thus, optical and terahertz spectroscopy methods complement each other in determination of the structural phase ratio in the $Nd_xGd_{1-x}Cr_3(BO_3)_4$ solid solutions. Based on the obtained data, we can claim that the $Nd_xGd_{1-x}Cr_3(BO_3)_4$ borates with $x \leq 0.2$ have essentially rhombohedral non-centrosymmetric structure (sp.gr. *R*32). This points to a possible existence of a considerable magnetoelectric effect in these compounds, the same as in non-centrosymmetric RE iron, aluminum and gallium borates. The next stage of the work is to prepare large crystals of the solid solutions with $x \leq 0.2$ for checking the magnetoelectric response.

This work was supported by the Russian Science Foundation (Grant No 14-12-01033). E.A.D. acknowledges a Scholarship of the President of the Russian Federation (SP-754.2015.1).

References

1. E.A. Popova et al., Phys. Rev. B **75**, 054446 (2007)
2. K.N. Boldyrev, E.P. Chukalina, N.I. Leonyuk, Phys. Sol. St. **50**, 1681 (2008)
3. L. Gondek et al., J. Sol. St. Chem. **210**, 30 (2014)
4. V.S. Kurazhkovskaya et al., J. Struct. Chem. **52**, 699 (2011)
5. E.Yu. Borovikova et al., Vibr. Spectr. **68**, 82 (2013)
6. A.M. Kadomtseva et al., Low Temp. Phys., **36**, 511 (2010)